Supplementary Material (ESI) for Journal of Materials Chemistry

Coupling of MnZn-ferrite films onto electronic components by a novel solution process for high frequency applications

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Physical characterizations of as-prepared and heat-treated films

Fig. S1a shows the XRD patterns for the as-prepared and heat-treated samples, which indicated that there is no change in the crystal phase even after the heat treatment. Raman spectroscopy further supports this; the Raman bands (Fig. S1b) observed around 341 cm⁻¹ (T_{2g}), 488 cm⁻¹ (E_g) and 641 cm⁻¹ (T_{2g}) is characteristics for the MnZn-ferrites and were in agreement with the previous reports¹ that remains unchanged after the heat treatment. The XRD and Raman studies show that the overall structure was not changed. Further, Mössbauer spectroscopy and XAFS techniques are employed to observe the possible changes in the valence and site distribution of ions. Fig. S1c shows the Mössbauer absorption spectra at room temperature for the films. The typical sextets observed are characteristics for the spinel ferrite.²⁻⁴ As confirmed by comparing the relative areas covered by the sextets from the A to B sites, the Fe^{3+} ions occupy both the octahedral B sites and the tetrahedral A sites. Similar observations were made by other workers indicating a nonequilibrium cation distribution,⁵⁻⁹ especially in the case of low temperature preparations. From the Mössbauer spectroscopic studies (Fig. S1c), it is clear that the heat treatment did not have any impact on the valence and site distribution of the Feions. The XANES spectra for the as-prepared and heat-treated films at the Mn K-edge are shown in Fig. S1d. In general, at the main edge the ferrite have three peaks at E =6540, 6543 and 6549 eV, which are related to various 4p electronic states of Mn^{2+} and/or Mn^{3+} in the octahedral coordination and at the pre-edge peak around E = 6533eV can be assigned to the unoccupied states at the Fermi energy $E_{\rm F}$.¹⁰ A comparison of the edge position for our films with that for various Mn oxides from the literature¹⁰⁻ ¹⁴ showed that it is slightly higher than for MnO and lower than for Mn₃O₄. This indicates that the films contain some Mn³⁺ in addition to Mn²⁺. Since the heat-treated samples exhibited a similar absorption edge to that of the as-prepared, it can be presumed that there is no major change in the oxidation state of manganese.



Fig. S1. Various analysis of the as-prepared and heat-treated INC structured films: (a) X-ray diffraction patterns, (b) Raman spectra, (c) 57 Fe Mössbauer spectra taken at room temperature, (d) Normalized Mn *K*-edge XANES spectra.



Fig. S2. Permeability profiles for the INC structured films with varying *x* (dotted-line is for the heat treated film, when x=0.15).



Fig. S3. Permeability profiles for the INC structured films with varying y (dotted-line is for the heat treated film, when y=0.05).

References

¹ O. Yamashita and T. Ikeda, *J. Appl. Phys.*, 2004, **95**, 1743.

² A. H. Morrish and P. E. Clark, Phys. Rev. B: Condens. Matter, 1975, **11**, 278.

³ G. A. Sawatzky, F. Vanderwo and A. H. Morrish, Phys. Lett. A, 1967, A 25, 147.

⁴ G. U. Kulkarni, K. R. Kannan, T. Arunarkavalli and C. N. R. Rao, Phys. Rev. B: Condens. Matter, 1994, **49**, 724.

⁵ J. P. Chen, C. M. Sorensen, K. J. Klabunde, G. C. Hadjipanayis, E. Devlin and A. Kostikas, Phys. Rev. B: Condens. Matter, 1996, **54**, 9288.

⁶ C. Rath, S. Anand, R. P. Das, K. K. Sahu, S. D. Kulkarni, S. K. Date and N. C. Mishra, *J. Appl. Phys.*, 2002, **91**, 2211.

⁷ M. Taheri, E. E. Carpenter, V. Cestone, M. M. Miller, M. P. Raphael, M. E. McHenry and V. G. Harris, *J. Appl. Phys.*, 2002, **91**, 7595.

H. Yasuoka, A. Hirai and T. Takada, J. Phys. Soc. Jpn., 1967, 22, 174.

⁹ G. Bonsdorf, M. A. Denecke, K. Schafer, S. Christen, H. Langbein and W. Gunsser, *Solid State Ionics*, 1997, **101**, 351.

¹⁰ S. Sakurai, S. Sasaki, M. Okube, H. Ohara and T. Toyoda, *Physica B*, 2008, **403**, 3589.

¹¹ A. Espinosa, E. Cespedes, C. Prieto, M. Garcia-Hernandez, J. Rubio-Zuazo and A de Andres, *J. Appl. Phys.*, 2008, **103**, 07D129.

¹² K. W. Nam, M. G. Kim and K. B. Kim, *J. Phys. Chem. C*, 2007, **111**, 749.

¹³ F. Farges, *Phys. Rev. B: Condens. Matter*, 2005, **71**, 155109.

¹⁴ F. H. B. Lima, M. L. Calegaro and E. A. Ticianelli, *Electrochim. Acta*, 2007, **52**, 3732.